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厦门大学理学博士学位论文

表面金属纳米结构体系的电化学、STM针尖诱导和模板法构筑及其表征

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Electrochemical, STM Tip-induced, Template Synthesis Fabrication of Surface Metal Nanostructures

A Thesis
Submitted to the Graduate School in Partial Fulfillment
of the Requirements for the Degree of
Doctor of Philosophy

By

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摘 要

当物质的尺寸进入纳米级的尺度时，将出现量子效应、小尺寸效应和表面及界面效应而呈现出既不同于宏观物体、也不同于单个原子的奇异现象。纳米科学与技术是研究和利用这一尺度上物质特性的多学科交叉的前沿和热点领域。纳米材料是纳米科学技术的基本组成部分，它是由三维空间中至少有一维处于纳米尺度范围的基本单元构成的材料，这一基本单元称为纳米结构。纳米微粒、纳米管、纳米棒和纳米薄层等都是纳米结构。若将它们按规律有序排列，则可以组装出常规体系不具备的物性。它们不仅具有单个纳米粒子的各种效应，而且还将出现许多如量子耦合效应与协同效应等新现象。

运用化学和物理等多种手段实现纳米至原子尺度范围的有序表面纳米结构的人工和自然构筑，是从结构到性能表征、研究和利用其物理化学基本性质的必要前提。遵循能量最低原理的**自然构筑法**可大面积制备表面纳米结构，而利用各种局域作用的**人工构筑法**则可“由下而上”按意愿构筑各种表面纳米结构并进行有关原理性探索。

电化学沉积方法具有简便、控制灵活等特点，是大范围制备表面金属或半导体纳米结构的一种有效的**自然构筑法**。依据沉积金属与基底表面的相互作用，金属的电化学沉积可以发生在其热力学平衡电位以负的过电位或以正的欠电位区间。当沉积金属与基底表面不具有强的结合能时，该金属的电沉积将在过电位区发生。控制条件使其按**瞬时成核**的机理进行，可制备较为均匀的表面金属纳米颗粒。若沉积金属与基底表面存在强的结合能，则可在欠电位区生成金属的（亚）单层。由于金属欠电位沉积本质上是一种特殊的电吸附过程，所形成的金属（亚）单层吸附层的结构强烈地依赖于电极表面的结构以及溶液中其它物种吸附的影响，可视为金属的**电化学外延生长**过程。

SPM（STM或AFM）作为一强有力的表面分析工具不仅是观察、认识原子分子世界的工具，也是实现表面修饰，甚至进行原子、分子操纵的重要手段。SPM针尖与表面存在各种相互作用，是对被研究表面的一种局域微扰，这种微扰在温和的电化学和隧道偏压条件下便可诱导电极表面发生特定的局域电化学反应。据此，可逐点构筑表面纳米结构，是一种先进的**人工构筑法**。

多孔氧化铝模板法借助自然构筑法和人工构筑法的概念，先自然地形成具有纳米尺度

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的有序孔洞（道），再人为地用物理或化学的方法向其内注入所需的材料，可大面积制备大小或长径比可调的纳米点、纳米线或纳米管，被认为是一种低投入高产出的制备大面积纳米线阵列体系的有效方法，尤其适合用于制备直径为 15 – 100 nm 的纳米线阵列。

虽然目前对纳米材料研究已是如火如荼，但是固体表面纳米结构的制备和物理化学研究则仍然较为少见，因此，需要实验和理论方法的创新和发展。本论文运用电化学，电化学扫描隧道显微镜（ECSTM）针尖诱导和模板法自然地和人工地构筑表面纳米结构，从简单的金属纳米粒子体系，拓宽到按意愿构筑表面有序纳米粒子阵列，从一维的纳米粒子体系拓宽到有序二维纳米结构体系；同时运用 Raman 光谱和扫描电化学显微镜（SECM）等多种表面分析工具对有关纳米结构和性能进行初步的表征。主要研究内容和结果摘要如下：

一、 电化学瞬时成核法构筑 HOPG 表面 Au 纳米粒子

高序热解石墨（HOPG）电极表面具有原子平整度，可认为是理想的单晶碳电极。HOPG 具有非常低的表面自由能，因此与沉积金属原子之间的结合能很小。这时金属的电化学沉积将发生在过电位区，并将遵循三维岛状生长的模式（Volmer-Weber 模式）。控制条件可使金属电沉积按瞬时成核的机理进行。据此可制备尺寸较为均一、排列较为有序的表面 Au 纳米粒子阵列。我们从在 $HAuCl_4$ 溶液中 Au 向 HOPG 表面过电位沉积的成核和生长机理着手，借助轻敲模式原子力显微镜，探讨阶跃电位、基底处理等方面对 Au 纳米粒子的形成及其尺寸和形貌的影响，并用电化学方法和表面增强拉曼光谱（SERS）技术初步研究了 Au 纳米粒子体系的电催化性能和光学效应，主要结果归纳如下：

1) ***电沉积条件对 Au 纳米粒子尺寸和形貌的影响*** 轻敲力模式 AFM 研究表明，Au 在 HOPG 表面电沉积 60 s 后的尺寸和形貌按沉积电位分为四种情况：(I) 当电极电位控制在 0.3V（vs. SCE，下同）以正的电位范围，Au 粒子以各向同性方式生长，形成亚微米尺寸的半球形 Au 粒子，粒子密度很小并且在电极表面比较分散；(II) 电位在 0.3 V 附近，由于该电位处于该体系的零电荷电位附近，Cl^- 从电极表面脱附，Au 的沉积表现为各向异性生长，形成棱角分明的多面体 Au 纳米粒子；(III) 恒定电位在 0.3 V ~ -0.3V 时沉积得到尺寸减小至几十纳米的半球形 Au 粒子，但分布密度增大；(IV) 在-0.3

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V 附近，沉积受到氢气在表面轻微溢出的影响，从而避免相邻粒子的扩散区间内的相互交叠，沉积得到的 Au 纳米粒子的尺寸分布狭窄，是构筑 Au 纳米粒子体系的理想条件。

2）*表面 Au 纳米粒子的电催化行为及粒子尺寸的影响* 以乙二醇电氧化为探针反应，比较了不同尺寸 Au 纳米粒子的电催化效应。研究表明，控制一定的电沉积时间（60 s），在电位区间(I)内(0.5 V)沉积的亚微米级的 Au 颗粒不具有电催化的作用；在电位区间(III)和(IV)（0.3 V 以负）沉积的 Au 颗粒由于尺寸减小到 100nm 以下，表面原子数目增多，配位不饱和而存在许多悬空键，使得这些表面原子极不稳定，从而对乙二醇的氧化反应有一定的催化作用，氧化电位负移了 50 mV。

3) *表面 Au 纳米粒子的表面增强拉曼散射（SERS）效应* 利用吡啶作为研究该体系 SERS 活性的探针分子，在 0.3 V 以正的电位下（电位区间（I））构筑的 Au 粒子体系无法检测到 SERS 信号；在 0.3 V 以负的电位下沉积的 Au 纳米粒子尺寸减小，同时粒子间距也明显减小，可以检测到吡啶分子的较强 SERS 信号。研究表明，SERS 增强因子受到 Au 纳米粒子的尺寸、间距、形貌的显著影响。结合 AFM 实验的结果，估算出在 0V 沉积 60 s 后获得的亚单层纳米金粒子（粒子直径约为 nm）上的 SERS 增强因子为 $10^4 \sim 10^5$。该研究有助于研究纳米粒子的形态、间距与 SERS 活性之间的关系，进而深入认识 SERS 机理中的电磁场增强机理。

二、电化学外延生长法构筑表面二维金属纳米薄层和原子簇

二维金属薄膜在催化、能源、材料和防腐、环境保护等方面具有重要的意义。Pd 的金属薄膜有较强的质子还原和氢吸收能力，而 Sn 易于与其它金属形成合金，在无铅焊接、电镀等方面具有较强的应用背景，同时两种金属薄膜对有机小分子的氧化都具有一定的电催化作用，具有直接的应用价值。我们利用电化学外延生长原理，在 Au(111)和 Au(100)表面构筑二维 Pd 和 Sn 薄膜，并用电化学 STM 研究其形成过程及基底结构和阴离子对薄膜结构的影响，电化学 STM 研究表明：

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1) Pd 从 $PdSO_4$ 溶液中向 Au(111)电极表面上的电沉积时，先在欠电位区形成（1×1）满单层吸附，而 SO_4^{2-}则在其上形成（$\sqrt{3}\times\sqrt{7}$）R19^{o}的诱导吸附；随后 Pd 在过电位区继续沉积，形成第二层有序的 Pd 膜。当 Pd 的厚度超过两层后，表面缺陷位增多，转为三维岛状生长。Pd 在 Au（100）电极表面上的电沉积表现出与 Au(111)上显著不同的特点，即使在欠电位区间，Pd 的亚单层膜也不具有通常的有序结构，而团聚成直径为 2-3 nm 的原子团簇，生长更趋向于三维岛状模式。

2) Sn 从 $SnSO_4$ 溶液中向 Au(111)表面欠电位沉积的初始阶段受基底表面重构与否而表现出不同的行为：在未重构的 Au(111)（1×1）表面，Sn 在表面随机成核，其尺寸约束在 2~3 nm 而不受沉积时间的影响。Sn 在 Au(111)（$\sqrt{3}\times22$）重构表面的欠电位沉积，其成核过程发生在 fcc 区，随后沿重构线骨架方向（$[11\bar{2}]$）生长，最后向 hcp 区扩展，呈现出各向异性的生长特点。

由上可知， Pd 从 $PdSO_4$ 向 Au(111)（1×1）上的电沉积是制备高度有序的 Pd 单层或双层膜的理想方法，阴离子的共吸附是形成有序结构的重要原因；而 Au(100)（1×1）上的电沉积则可能是获得具有特殊催化活性的 Pd 原子团簇的有效方法。Sn 从 $SnSO_4$ 溶液中向 Au(111)表面欠电位沉积的尺寸约束或各向异性生长行为，则反映基底表面因重构而造成的几何和电子结构的微弱差异将引起电沉积行为的显著不同。上述研究结果与欠电位沉积理论中关于金属吸附原子有序结构的描述显著不同，具有重要的理论意义和实用价值。

三、电化学 STM 针尖诱导构筑表面有序 Pd 纳米粒子阵列及 SECM 电催化性的初步研究

为了按意愿实现纳米粒子在表面的构筑，我们选择具有催化活性的Pd为对象，用STM技术的“ jump to contact ”原理在Au单晶电极表面构筑大小、高度和间距可调的Pd纳米粒子阵列，并研究其在不同介质中的稳定性；首次尝试具有电化学灵敏性的SECM技术与电化学STM技术的联用，检测所构筑的Pd纳米粒子阵列的电化学活性，为更好地解释金属纳米粒子的电化学行为奠定实验方法。初步结果归纳如下：

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1) 利用STM“ jump to contact ”原理，在Au(111)单晶电极表面构筑了直径为几个纳米的Pd粒子阵列；构筑过程中，通过调节压电陶瓷管Z方向上所加的电压脉冲，可以控制纳米粒子的高度在二到四个的单原子层内。

2) 含Cl^-和含SO_4^{2-}溶液中都可以在Pd的UPD电位之前构筑稳定的Pd纳米粒子。在含Cl^-溶液中，由于$PdCl_4^{2-}$在Au(111)表面的强吸附，有可能对后续测量带来干扰；而在$PdSO_4$溶液中，Pd纳米构筑虽然需要的时间明显延长从而增加了纳米构筑的困难，但可避免离子吸附对后续研究的干扰。

3) 通过设计电化学STM和SECM流动电解池，可成功地转换构筑的纳米粒子所处的环境。Pd纳米粒子稳定性研究表明，在支持电解质溶液（H_2SO_4溶液）和空气中，Pd纳米粒子高度在数小时内高度恒定不变，为进一步的SECM电活性表征奠定了实验基础。

4) 首次尝试STM与SECM的联用，以质子的还原－氧化反应为探针反应，利用SECM基底产生/针尖收集模式，研究Au电极表面有序Pd纳米粒子阵列对质子还原的能力。SECM实验检测到Pd纳米粒子阵列上析氢反应的电化学信号，实验尚需进一步完善。

四、氧化铝模板法构筑金属纳米线阵列

金属纳米线属于一维纳米材料，可用于构筑纳米器件和超大集成电路中的连线，准一维纳米材料在介观领域和纳米器件研制方面有着重要的应用。利用模板法可以按需在模板中组装各种人们需要的一维纳米材料，而纳米线的直径和长度及表面有序性与模板孔洞的尺寸和有序性密切相关。我们以阳极氧化铝为模板，摸索了尺寸可控而有序性高的模板的制备条件及影响因素；比较了交、直流法在氧化铝模板中电沉积的特点和优势，在模板孔洞内合成 Au 和 Cu 纳米线，并利用 AFM、SEM 和 TEM 等技术其进行表征；利用 SERS 技术表征金属纳米线阵列的电子性质。主要结果如下：

1) *氧化铝模板的制备*　通过改变氧化电压、电解质和温度，可获得孔径具有15 nm至 90 nm的一系列多孔氧化铝模板；通过电化学氧化的两步法获可良好的初始氧化表面，可有效

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提高多孔氧化铝模板中孔道结构的有序性。

2） ***交、直流电沉积法制备金属纳米线*** 交流电沉积法适合直接在含氧化铝阻挡层（绝缘层）的模板中进行沉积，操作简单方便。但由于电沉积所需的电压较大，阴极过程中析氢与金属离子的还原过程相互竞争，难以准确控制金属沉积过程及形成纳米线的长度。直流电沉积法在一面已镀上导电金属的穿透的氧化铝模板中进行，可用恒电流法在很小的电流密度下制备致密、均匀并且连续的金属纳米线。

3） ***金属纳米线阵列的SERS表征*** 选择SCN^-作为该研究的探针分子，通过部分溶解氧化铝模板控制金属纳米线露出氧化铝模板的高度，原位记录溶解过程的SERS谱图。较系统地分析一系列不同直径、不同金属纳米线阵列的SERS光谱。发现在开路电位下，当Cu纳米线直径小于50 nm 时，探针分子频率随纳米线直径减小而明显降低。相应的理论计算分析表明，造成该有趣现象的原因可能是纳米粒子的小尺寸效应和表面效应所致，前者导致金属纳米线的费米能级随直径减小而升高，后者导致金属纳米线表面活性增高。金属纳米线的电子性质改变使表面电子更容易给予探针分子而造成其频率的位移。

总的来说，本论文运用电化学、ECSTM 针尖诱导和氧化铝模板法对自然和人工地构筑表面金属纳米结构体系做了多方面的尝试，并从中发现了一些新的现象。由于在论文工作期间，因需要而参与了两个国际合作课题，导致了课题内容的多样性和复杂性。并且由于时间上的限制，所得到的结论是初步和尚不十分完整的，需要进一步实验和完善。例如在 STM 和 SECM 联用的实验中，虽然我们克服了针尖定位、溶液交换等许多困难，SECM 获得的有关 Pd 纳米粒子对质子还原行为的研究结果仍然有待进一步考证。同时，应当结合更多其它技术对制备的纳米结构体系作全方位的表征，进而促进对纳米结构和纳米材料的深入理解和更好的应用。

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ABSTRACT

When the size of a substance is reduced to nanometer scale, several phenomena such as quantum confinement effect, small size effect, surface and interface effect may appear, which make the substance significantly different from its bulk or single atoms in physical and chemical properties. Being a disciplinary of many subjects, nanoscale science and technology (Nano-ST) includes fundamental research of properties in nanometer scale and application of the functional nano-materials, and has boomed up as the hottest field and frontier of science. Nano-material is composed of basic building block termed as nanostructure with at least one dimension in the nanometer range, nanoparticle, nanowire(rod), nanorod and thin film being such nanostructures. Assembly of the nanostructures into a system in a certain order would lead to some novel properties due to coupling between the nanostructures in addition to the above-mentioned four types of effects.

Synthesis of nanostructures is the prerequisite of applying, investigating and utilizing the physical and chemical properties of these nanostructures. The present available physical and chemical methods in nanostructuring can be categorized into **nature-driven** and **man-driven** ones. The ***nature-driven nanostructuring process*** could produce surface nanostructure in large area following the minimum energy principle; while the ***man-driven nanostructuring process*** makes use of localized effect to fabricate surface nanostructures following the “bottom up” procedure, which is particularly useful in exploring novel property of the nanostrucutes.

The convenient and flexible electrochemical deposition method is one of the efficient ways to fabricate metal and semiconductor nanostructures. Depending on the interaction between the depositing metal and the substrate, the metal deposition could take place at potentials negative of the equilibrium potential of the metal (over potential deposition, OPD) or positive of that equilibrium potential (under potential deposition, UPD) .In the absence of strong metal-substrate interaction the metal deposition will take place in the OPD region. If the deposition process can be controlled following the instantaneous nucleation mechanism, uniformly distributed metal nanoparticles is expected to form on the surface. In the presence of strong metal-substrate interaction, however, a (sub) monolayer of the metal will be formed in the UPD region before further its OPD. UPD is a special adsorption process of metal; the morphology of the metal monolayer is strongly influenced by the surface structure of the electrodes, the ionic adsorption

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and electrode/solution double layer structure, which can be regarded as electrochemical epitaxy process.

As an important surface analyzing tool, well-developed STM technique has been employed not only as an important tool to characterize the arrangement of atoms and/or molecules on the surface but also as a lithographic means to direct the individual atoms and molecules to the predetermined position on the substrate with the tip. Tip-substrate interaction of various kinds is regarded as a local perturbation that may induce local electrochemical reaction under mild conditions of tunneling current and voltage. Thus, the surface nanostructure could be fabricated point by point and serves as an advanced man-driven nanostructuring process.

Template synthesis method for example anodic aluminum oxide (AAO) is based on the combination of two kinds of methods. The nano-channel arrays are formed spontaneously during anodization, and materials are filled into the nano-channels arrays purposely by chemical or physical methods to synthesize nanowire (rod) or nanotube arrays with different diameter and aspect ratio in a large scale. It is regarded as one of the low-input and high-output methods to fabricate metal nanowire arrays especially with the diameter ranging from 15 nm to 100 nm.

1. Electrochemical instantaneous nucleation and preparation of Au nanoparticles on HOPG

The atomically flat HOPG (highly oriented pyrolytic graphite) electrode with low surface energy is considered as an ideal single crystal substrate of carbon. The weak interaction between the substrate and electrodeposited metal resulted in the metal deposition process with the three-dimensional island growth mode (Volmer-Weber mechanism) in the OPD range. By controlling the experimental condition, the Au nanoparticles arrays on HOPG with uniform size distribution could be obtained. In the present thesis, the kinetics and mechanism of gold electrodeposition on HOPG is studied by potential step method combined with tapping mode AFM (TM AFM) as an ex-situ tool to characterize the Au nanoparticles. The influences of the step potential, deposition time and pretreatment of the HOPG surface on the formation and morphology of Au nanoparticles are discussed. Investigations of electrocatalytic and optical properties have been carried out by electrochemical method and surface enhanced Raman spectroscopy (SERS), respectively. The main results are as follows:

1) Effect of electrochemical deposition condition on the size and morphology of the Au

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nanoparticle

TMAFM results indicate that the size and morphology of Au nanoparticles after deposition for 60s can be outlined into four situations in terms of the deposition potential:

（I） At potentials positive of 0.3V vs. SCE, the isotropic growth of Au leads to the hemispherical formation of Au particles with low density on HOPG;

（II） At the potential nearby 0.3V, which is close to the **pzc** (potential of zero charge) of the Au in the system, the Au particles change from hemispherical to polyhedral morphology. The phenomenon is attributed to be related with desorption of chloride from the Au nanoparticles at around this potential.

（III） In the potential range between 0.3V and -0.3V, densely distributed hemispherical particles prevail with sizes about several tens nanometers.

（IV） At more negative potential nearby –0.3V, the formation of Au nanoparticles benefits the slight hydrogen evolution, which prevents from coalescing of the diffusion layers of the adjacent nanoparticles. In this case, the deposited Au nanoparticles possess narrow size distribution and were well separated from each other. This potential appears to be the ideal condition to fabricate ordered Au nanoparticles array.

2) Size dependent electocatalytic properties of the Au nanoparticles

Glycol eletrooxidation is used as a probe to examine the electrocatalysis of Au nanoparticles on HOPG. Au nanoparticles prepared under the condition (I) (0.5V) with submicrometer size do not show any electrocatalytic activity. Those prepared under the condition (III) and (IV) with size below 100nm show electrocatalytic activity. Compared with that on Au large microparticles, the initiation of the glycol oxidization is about 50mV more negative, which is likely due to the increased surface atoms rich of dangling bond.

3) SERS effect of the Au nanoparticles

Using Pyridine as a sensitive SERS molecule to probe the electronic properties of the Au nanoparticles. No signals are detected from the Au particles prepared in potentials positive of 0.3V. However, Au nanoparticles prepared at potentials negative of 0.3V with decreasing size and distance between the nearest nanoparticles, SERS signal could be detected from. An enhancement factor of 10^4-10^5 is estimated for Au nanoparticles prepared at 0V. The preliminary results indicate that Au nanoparticles of varying size, shape and distance of the nanoparticles on HOPG can be used as a model system to help reveal the SERS mechanism.

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2. Electrochemical epitaxial growth of metal monolayer and thin film on Au

Metal thin films have attracted considerable interest in relation to catalysis, energy, material, corrosion and environmental protection. Pd thin film is capable of proton reduction and strong hydrogen absorption, while Sn can easily alloy with other metals and is used intensively in electroplating and soldering industry. Both metal show electrocatalytic activity to the oxidation of small organic molecules. In this thesis, one or two monolayer Pd or Sn thin film are prepared on Au single crystal via electrochemical epitaxial deposition. In-situ STM measurements are performed to study the deposition process and the influence of the surface structure and anion adsorption.

1) When Pd is deposited from $PdSO_4$ solution on Au (111) in the UPD range, a monolayer of Pd with pseudomorphic (1×1) structure was formed on the substrate with induced ($\sqrt{3}\times\sqrt{7}$) R19° SO_4^{2-} adsorption. With decreasing potential the OPD range, the second pseudomophic monolayer is formed with induced SO_4^{2-} adsorption similar to that on the first monolayer. When the Pd reaches more than two monolayers, the deposition process change to follow three-dimensional growth model with increased defects. The growth of Pd on Au (100) differs significantly from that of Pd on Au (111). Even in the UPD range, size-confined 2-3 nm clusters are observed but ordered adlayer.

2) Deposition of Sn from $SnSO_4$ solution on reconstructed and unreconstructed Au (111) surfaces differs significantly. On the unreconstructed Au (111) surface, Sn forms size-confined two-dimensional clusters of 1-2 nm. While on reconstructed Au (111) surface, Sn prefers to nucleate in the face-centered cubic regions followed by anisotropic growth along the $[11\bar{2}]$ direction of the reconstruction rows. The nuclei expand towards the hexagonal close packed regions to build up deposit domains.

As mentioned above, Pd deposition from $PdSO_4$ on Au (111) (1×1) is the ideal way to fabricate one or two monolayers of Pd film, in which induced anion adsorption on Pd film could play an important role. Pd deposition on Au (100) could be one of the methods to fabricate catalytically active Pd clusters with confined size of 2~3 nm. Sn UPD deposition from $SnSO_4$ possessed the size-confined effect or anisotropic growth behavior, which reflects the electronic and structural influence of the two surfaces. The above results show discrepancy with other UPD systems, in which ordered adlayer structures are observed.

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3. STM tip-induced nanostructuring of Pd cluster arrays and preliminary electrocatalytic investigation with SECM

STM has been employed to fabricate catalytically active Pd nanocluster array with tip-induced method. By varying the voltage applied to the z-piezo, the height of the nanocluster and the distance between them could be adjusted. The stability of the Pd nanoclusters in different electrolytes is also investigated. For the first time, the combination of SECM with STM has been attempted to detect the electrochemical activity of Pd nanocluster array. The preliminary results are as follows:

1) Based on the “jump-to-contact” mechanism of STM tip-induced method, metal nanoclusters with the diameter of several nanometers can be fabricated on Au single crystal electrodes. By adjusting the voltage applied in the Z-direction of piezo, the height could vary from 2 to 4 monolayers.

2) In both H2PdCl4 and PdSO4 electrolytes, large and stable Pd cluster arrays are fabricated at potentials positive of Pd UPD potential. Based on the consideration that strong adsorption of $PdCl_4^{2-}$ in the chloride containing solution would introduce contamination in the follow-up combined SECM measurements, Pd nanostrucuring from $PdSO_4$ is preferred although 20 times longer “waiting time” is necessary for Pd supply to the tip.

3) By designing a suitable solution changing system, Pd cluster arrays are successfully transferred to air or H_2SO_4 solution, which is a necessary procedure for further SECM measurement. No change is observed for the Pd nanoclusters after transferring into air and the height of the Pd clusters remains constant for tens of hours. This ensures possibility to carry out the SECM measurements with such Pd nanocluster arrays.

4) Successive SECM measurements use the proton reduction-oxidation reaction as a probe to detect the faradic current of the SECM tip in the “substrate generation-tip collection” mode. Preliminary results indicate an active signal from the proton reduction on the Pd nanocluster arrays but further investigation is necessary.

4. Fabrication metal nanowire arrays with AAO template synthesis method

Metal nanowire belongs to one-dimensional nanomaterial, which could be applied in the fabrication of nanodevice and connective wire in the immense integrated circuit. By using the template synthesis method, one-dimensional material could be willingly assembled into the

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